

Studies of the Processes Operative in Solutions. XXVII.—The Causes of Variation in the Optical Rotatory Power of Organic Compounds and of Anomalous Rotatory Dispersive Power.

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Biot, the distinguished French physicist, to whose genius we owe the discovery, in 1815, of the property now spoken of as optical rotatory power, made the further discovery that certain substances in solution, notably tartaric acid, offer an exception to the rule that the deviation which a polarised ray undergoes in its passage through a liquid is greater the shorter the wave-length. The precise manner in which variation takes place was established by Arndtsen,* who determined the rotatory power of solutions of tartaric acid using light of the refrangibility of the lines *c*, D, E, *b*, F, *e* of the solar spectrum.

In calling attention to these observations, in the article "Light" in the third Supplement of Watts' 'Dictionary of Chemistry,' published in 1881, one of us pointed out (p. 1208) that—

"Two optically active, chemically indifferent bodies of opposite rotatory power, having *different rotatory dispersive powers*, if mixed in certain proportions, would (as Biot has shown for a solution of dextrorotatory camphor in levorotatory turpentine oil) exhibit phenomena similar to those manifested by tartaric acid solutions; hence the most probable explanation of the anomalous rotatory dispersive power of solutions of tartaric acid would appear to be that they contain, besides the acid, a compound of opposite rotatory power of the acid with water, in proportions varying according to the concentration and temperature of the solutions."

But that this explanation was not regarded as altogether satisfactory is apparent from a sentence written at about the same time which appears in the edition of Miller's 'Elements of Chemistry,' Part III, "Organic Chemistry" (p. 992), published in 1880:—

"The anomalous rotatory dispersive power of aqueous solutions of tartaric acid almost necessitates the assumption that the acid forms a compound with water opposite to itself in rotatory power; the formation of a body having a reversed rotatory power as compared with that of the parent substance from a compound like dextrotartaric acid, which, according to Van't Hoff's hypothesis, has the constitution 2A—*i.e.*, is composed of two similar dextrorotatory groups—is, however, not easy to understand."

In those days, of course, our knowledge of structure was far less developed than is now the case. Meanwhile, notwithstanding the attention devoted to the study of optically active substances since the introduction of Van't Hoff's

* 'Ann. Chim. Phys.,' 1858, (3), vol. 54, p. 415.

masterly generalisation in 1875,* until recently it has been customary only to determine rotatory power in yellow light. The simplification and improvement of the polarimeter effected by W. H. Perkin, senior, who was the first to develop the method originally devised by Fizeau and Foucault in 1845, by using a spectroscopic eye-piece, undoubtedly gave an impetus to the use of light of other degrees of refrangibility. T. M. Lowry has since improved the method and by the use of photography has extended it so that the measurements can now be made without difficulty not only in the visible but also throughout the ultra-violet region;† this work, it may be added, was undertaken mainly in consequence of the suggestion made to him by one of us several years ago that it was desirable to reinvestigate the subject of anomalous rotatory dispersion from the point of view of Biot's suggestion.

The method has been in use during several years past in our laboratory and in that of Prof. Pope.

It is safe to say that it is no longer legitimate to confine the measurements of rotatory power to yellow light.

It is remarkable that so little attention should have been paid to rotatory dispersive power and to the anomalous behaviour of some substances. Walden, in his comprehensive survey of the subject of optical activity, in the lecture he delivered to the German Chemical Society in 1905,‡ mentions almost casually the abnormal behaviour of tartrates without reference to Biot's explanation and this has been disregarded also by Frankland, Patterson and other recent workers, even by Winther, who has discussed change in rotatory power particularly in relation to the changes in the "solution-volume" and the "internal pressure" of solutions.§ Winther, following Biot, considers that abnormalities in dispersive power are due to the presence of forms differing in rotatory power but supposes that these are complex molecules and compounds of solute and solvent.

The effect of solvents on the rotatory power of certain tartrates has been made the subject of most exhaustive study during the past 12 years by T. S. Patterson, who, in a series of 20 communications to the Chemical Society, has shown that different liquids produce extraordinarily different effects in changing the rotatory power especially of tartrates.

He has recently|| summarised the results which he and others have obtained

* Compare Frankland, Presidential Address, 'Chem. Soc. Trans.,' 1912, p. 654.

† 'Phil. Trans.,' 1912, A, vol. 212, p. 261.

‡ 'Berichte,' pp. 366-408.

§ 'Zeit. Phys. Chem.,' vol. 60, pp. 563, 590, 641, 756.

|| An attempt to harmonise qualitatively the relations between temperature and rotation for light of all refrangibilities of certain active substances both in the homogeneous state and in solution, 'Chem. Soc. Trans.,' 1913, p. 145.

but without arriving at any more definite conclusion as to the cause of the variations observed than that involved in the statement—

“it may be possible to explain all these facts in terms of the very popular, if somewhat vague—or because somewhat vague?—ideas, association or complex formation—solvation—and it would be exceedingly interesting if some exponent of these ideas would attempt to show that it is possible to formulate a consistent scheme based on them and capable of withstanding even the first breath of criticism but to the author it appears that the potentialities of the asymmetric carbon atom and of the most simple physical conception of those intermolecular forces to which liquefaction is due are ample to account for all the observed behaviour.”

Apart from the difficulty of understanding what is implied in the expression “the potentialities of the asymmetric carbon atom and of the most simple physical conception of those intermolecular forces to which liquefaction is due,” this pronouncement does not carry us very far.

The position is well summarised in the December number of the Chemical Society’s ‘Transactions’ (p. 2313), by Pope and Winmill, in the following statement:—

“It may here be noted that the variability of rotation constants with solvent was attributed by Pope and Peachey (‘Trans.’ 1889, vol. 75, p. 1111), in the main, to changes in association of the optically active substance produced by the solvent; Patterson opposed this view (‘Trans.’ 1901, vol. 79, p. 186) and strongly advocated the idea that the cause of variation of rotation constant with solvent is to be found in variation of the internal pressure prevailing in the solution. Patterson’s later papers indicate that he has abandoned the view that internal pressure is an operative factor in connexion with variations in the rotatory power, whilst Walden (‘Ber.’ 1905, vol. 38, p. 345) apparently adopts the view, that, in the main, the association factor determines the rotatory power. The complex character of the problem under discussion discourages any attempt to draw a final judgment between the several views which have been advanced as guides to further investigation.”

It has long been obvious that the inquiry into the processes operative in solutions which is the subject of this series of studies would be incomplete if changes in optical rotatory power such as have been referred to were not considered. The observations recorded in the previous communication of the series (XXVI),* in which the passage from the lævorotatory to the dextrorotatory form of fructose is discussed, have so direct a bearing on the problem that we have been led to give the matter special consideration.

In considering the literature of the subject, our attention was at once attracted by a recent account given by Pope and Winmill (*loc. cit.*) of the optical properties of tetrahydroquinaldine and various derivatives of this compound. It is pointed out by these authors that the orthonitrobenzoyl-derivative has quite abnormal rotatory constants and that its rotatory

* “The Disturbance of the Equilibrium in Solutions of Fructose by Salts and Non-electrolytes,” by E. E. Walker, ‘Roy. Soc. Proc.’ 1913, A, vol. 88, p. 246.

dispersive power is anomalous; the mean values for the latter which they record are as follows :—

Table I.

	Alcohol.	Benzene.	Acetone.	Acetic acid.
Hg green/Na yellow	−0·1181	+1·701	−1·213	+0·483
Hg yellow/Na yellow	+0·805	+1·147	+0·4995	+0·917

It will be observed that the variation in the dispersion coefficient brought about by a change of solvent is very great. 2-Nitrotoluene-4-sulphonyl-tetrahydroquinaldine is equally abnormal in its behaviour; moreover, in the case of this compound, benzene has most and acetone least effect on the rotatory power, which is a complete reversal of the order of effect observed in the case of nine other derivatives similar to these two compounds which were studied; these behave normally, though the rotatory power of each varies greatly according to the solvent used: in the case of each compound the rotatory dispersive power is the same whatever the solvent used. It is obvious that a special explanation is required to account for the peculiar behaviour of the two compounds mentioned.

Discussion of Special Cases and Construction of Characteristic Rotation-Dispersion Diagrams.

The optical properties of a liquid substance or of a solution consisting of two isodynamic forms of different rotatory power may be represented graphically in a very simple manner, as shown in fig. 1, in which the following four cases are represented :—

Case I. Two substances having rotatory powers of the same sign and the same dispersive power.

Case II. Two substances having rotatory powers of the same sign but different dispersive power.

Case III. Two substances having rotatory power of opposite sign but the same dispersive power.

Case IV. Two substances having rotatory power of opposite sign and also different dispersive powers.

In the diagram, specific rotatory power is represented by the ordinates and percentage composition by the abscissæ. It is assumed that the rotatory power of each of the two constituent isomers is constant under all conditions; the extent to which this assumption is justifiable will be discussed later on when various actual examples have been considered.

R_1 , G_1 , B_1 , represent the specific rotatory power of the one form on using red, green and blue light respectively, R_2 , G_2 and B_2 have the same significance for the isomeric form. The diagrams are self-explanatory. It is only necessary to point out that only compounds coming under Case IV are likely to occasion anomalous dispersion; the region in which the dispersion is anomalous lies between the two dotted lines in the diagram.

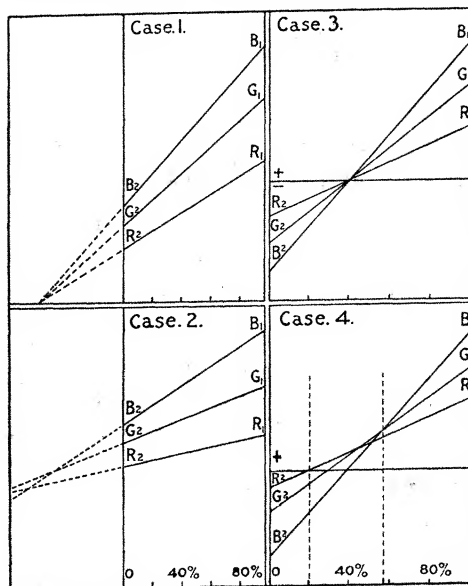


FIG. 1.—Rotation-composition diagrams.

Fructose.—Passing from ideal cases to actual facts, the case of fructose may now be considered. There is every reason to suppose that this compound is present in solution in two isodynamic forms and it has been shown in Part XXVI of these studies that the proportions in which these are presumably present in equilibrium may be altered to a considerable extent by the addition of alcohol or other substances. In order to determine under which of the above four cases fructose comes, a solution was made up containing two molecular proportions of fructose and 100 molecular proportions of water and the rotatory power of this solution was determined using the light of the yellow, green and blue lines emitted by a mercury vapour lamp. Various quantities of alcohol (containing 0.73 per cent. water) were then added and the specific rotatory powers determined as before. The results are given in Table II.

It will be noticed that the values given in the last two columns representing the dispersion are practically constant, except in the most dilute solution in which the experimental error is large.

This result is of importance in proving that the dispersion may be normal even when more than one form is present, a conclusion of moment as Winther appears to consider that when the dispersion does not vary it is to be supposed that only one substance is present in solution; in such cases he ascribes the changes in rotatory power merely to the alteration of the internal pressure.

Table II.

Molecular proportions of alcohol per 100 of water.	α_{Yellow}	α_{Green}	α_{Blue}	$[\alpha]_{\text{Y}}^{25}$	$[\alpha]_{\text{G}}^{25}$	$[\alpha]_{\text{B}}^{25}$	$\frac{\alpha_{\text{G}}}{\alpha_{\text{Y}}}$	$\frac{\alpha_{\text{B}}}{\alpha_{\text{G}}}$
0.00	-66.503	-75.230	-124.38	-93.73	-106.03	-175.29	1.1312	1.653
9.28	49.557	56.080	92.56	87.08	98.55	162.65	1.1316	1.651
24.65	34.279	38.794	64.15	80.13	90.69	149.62	1.1317	1.654
54.9	20.903	23.654	39.10	73.50	83.17	137.48	1.1316	1.653
167.0	9.059	10.255	16.98	64.22	72.52	120.59	1.1322	1.656
1724.0	0.700	0.786	1.32	49.7	55.7	93.7	1.12	1.68

The values for blue light cannot be regarded as so nearly accurate as those for yellow and green; on account of the spectroscopie being in the eye-piece of the polarimeter, the flood of yellow and green light is so great that when the rotation is considerable the blue is obscured. Therefore in the case of solutions 1 and 2, a blue filter was used to cut out the yellow and green bands; unfortunately this rendered the blue fainter also.

If the assumption be made that the composition of the mixture studied is a linear function of the specific rotatory power in the case of a given coloured light, all the points representing the specific rotatory power in other colours should fall on straight lines when placed on the appropriate ordinates; the abscissæ should then represent the composition to an unknown scale. To construct the diagram characteristic of a substance, a *reference line* is drawn with a slope of unity and on this are plotted the various specific rotations of light of any one of the refrangibilities observed. The points for other refrangibilities are then plotted on the ordinates passing through the points previously located on the reference line. The observations may be those made either at different temperatures or in different solvents or at different concentrations.

It is proposed to call the portion of the rotation-composition diagram drawn in the manner described the *Characteristic Diagram*, as it shows under which of the cases discussed on p. 391 the substance comes.

When the characteristic diagram of fructose (fig. 2) is drawn from the data given in Table II, it is clear that this sugar comes under Case III and that it is to be supposed therefore that the two isodynamic forms have the

same dispersive power. Glucose, in all probability, would come under Case I, as both the α and β forms are positive and presumably equally dispersive.

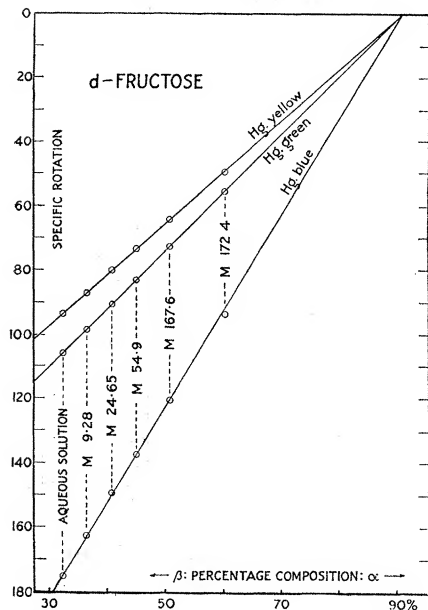


FIG. 2.—Characteristic diagram of *d*-Fructose. Equilibrium between α and β forms altered by the addition of alcohol to the aqueous solution. Reference colour, Hg green.

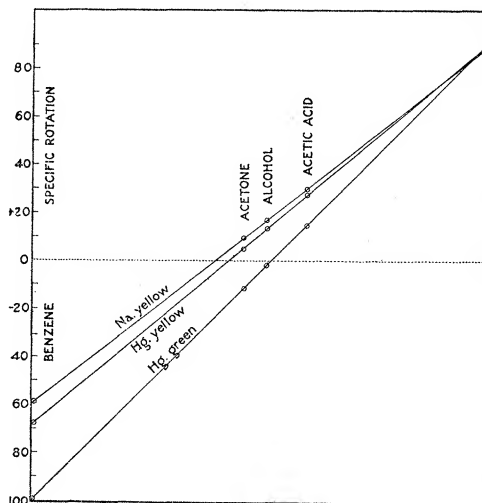


FIG. 3.—*o*-Nitrobenzoyl-1-tetrahydroquinaldine. Equilibrium varied by change of solvent at constant temperature 20° C. Reference colour, Hg green.

In cases in which the rotatory powers of the separate forms are unknown the composition cannot be inferred; but in a case such as that fructose affords it is possible to attach a scale to the axis of abscissæ, assuming that the rotatory power of each form is the same at all dilutions.

According to Hudson, the specific rotatory power of the two forms of fructose are $[\alpha]_D = +17^\circ$ and -140° . The corresponding mercury green values deduced by extrapolation from the dispersion curve may be taken as $+20^\circ$ and -165° . Using these values, the rotations in green light corresponding to various percentages may be directly calculated.

Any substance which has a variable rotatory power but constant dispersive power would be represented by a similar diagram.

o-Nitrobenzoyltetrahydroquinaldine.—The mean specific rotatory powers of this substance in various solvents are as follows:—

Table III.

Solvent.	$[\alpha]_D$	$[\alpha]_{\text{Hg yellow}}$	$[\alpha]_{\text{Hg green}}$
Alcohol	+ 2°017	+ 13°77	+ 17°11
Benzene	— 99°30	— 66°97	— 58°37
Acetone	— 11°73	+ 4°83	+ 9°67
Acetic acid	+ 14°50	+ 27°50	+ 30°00

The characteristic diagram (fig. 3) constructed from these data and the dispersion values previously cited shows that this substance is to be regarded as coming under Case IV. The slope of the lines is no longer a measure of the dispersion as it is in the case of fructose but gives what is practically identical with Winther's "solution dispersion coefficient."*

The value of this coefficient calculated from the various pairs of solutions is remarkably constant in comparison with the apparently irregular variation of the dispersion coefficient (*cp.* Tables I and IV).

Table IV.

	$\frac{\Delta[\alpha]_{\text{Hg green}}}{\Delta[\alpha]_{\text{Hg yellow}}}$	$\frac{\Delta[\alpha]_{\text{Hg green}}}{\Delta[\alpha]_{\text{Na yellow}}}$
Alcohol and benzene	1·215	1·289
Acetone and benzene	1·220	1·287
Acetic acid and benzene.....	1·232	1·288
Acetic acid and alcohol	1·232	1·281
Point of intersection	84°8'	83°7'

* Winther ('Zeit. Phys. Chem.,' vol. 41, p. 207) has shown that the increase in the rotatory power of the ethereal salts of tartaric acid can be represented as a parabolic function of the temperature

$$[\alpha] = a + b(t - 149).$$

If b_1 and b_2 are the values of b for light of two different wave lengths, then Winther called the ratio b_1/b_2 the rational dispersion coefficient; this was shown to be to a large extent independent of the concentration and the solvents. Subsequently, he (*ibid.*, vol. 45, p. 373) used what he termed the "solution-dispersion coefficient"; this was calculated from the expression:—

$$\Delta[\alpha]_a/\Delta[\alpha]_b$$

where $\Delta[\alpha]_a$ and $\Delta[\alpha]_b$ are the changes in rotatory power of light of two different wave lengths occasioned by a given change in concentration. (The "rational dispersion coefficient" was determined from a similar expression when the constants of the parabolic equation were not known.)

It is clear that this latter ratio is identical with the ratio of the slopes of the lines of the characteristic diagram; in fact the slope of these lines represents this quantity

Methylic Tartrate.—Methylic tartrate may be taken as a third example. Probably more work has been done on the rotatory power of the ethereal salts and other derivatives of tartaric acid than of any other group of compounds; there are therefore ample data for purposes of discussion: nevertheless it was thought desirable to make a set of experiments similar to those made with fructose, in order to compare the effects produced in the two cases. The rotation was measured in the yellow, green, blue-green and blue light of the mercury lamp spectrum; it was impossible to measure the blue-green very accurately on account of its extreme faintness but the values show the trend of the curve sufficiently well and are included in the diagram. The solution contained 1 gramme molecular proportion of tartrate to 100 of water and the number of gramme molecules of alcohol recorded in the table.

Table V.

Molecular proportions of alcohol per 100 of water.	α_{Yellow}	α_{Green}	$\alpha_{\text{Blue-green}}$	α_{Blue}	$[\alpha]_{\text{Y}}^{25}$	$[\alpha]_{\text{G}}^{25}$	$[\alpha]_{\text{BG}}^{25}$	$[\alpha]_{\text{B}}^{25}$
0.00	+7.676	+8.443	+9.77	+11.32	+19.01	+20.91	+24.19	+28.04
8.91	5.494	6.025	6.86	7.95	16.28	17.85	20.32	23.55
22.20	3.487	3.778	4.29	4.60	12.56	13.61	15.45	16.57
52.0	1.758	1.865	2.06	1.94	10.60	11.23	12.42	11.70
128.8	0.650	0.673	0.65	0.43	7.51	7.76	7.51	4.96

The characteristic diagram (fig. 4) drawn from these data shows that methylic tartrate also comes under Case IV. The comparatively low values at which the lines cross is probably an indication that there is considerably less difference between the magnitude of the dispersion of the two forms than in the case of the quinaldine derivative and probably also a correspondingly smaller difference in constitution.

A point of great significance in this diagram is the fact that the values for the ethereal salt alone at various temperatures lie practically on the projection of these curves, the whole forming one complete diagram. These values were deduced from Winther's data* by graphic interpolation from the dispersion curves; the values so obtained are given in Table VI.

directly when the line of unit slope is chosen as denominator. It therefore appears desirable to designate the ratio:—

$$\Delta[\alpha]_a/\Delta[\alpha]_b$$

by a single term, whether the change in equilibrium be caused by an alteration either in temperature or in concentration or solvent; for this purpose the term "rational dispersion coefficient" might well be retained.

* *Op. cit.*, vol. 41, p. 176.

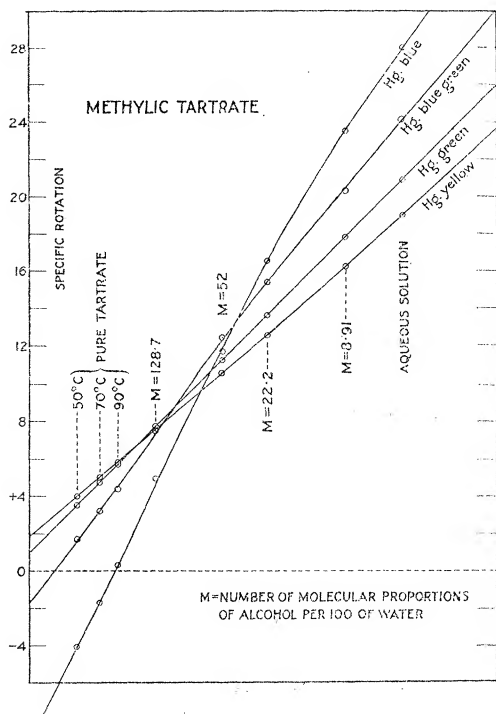


FIG. 4.—Equilibrium varied by the addition of alcohol to the aqueous solution and by heating the original substances.

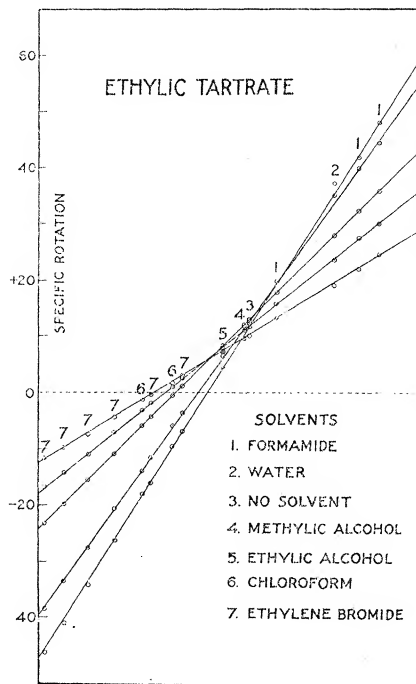


FIG. 5.—Ethylic tartrate. Equilibrium varied by change of solvent and concentration at constant temperature 20° C.

Table VI.

Temperature.	$[\alpha]_D^{20}$	$[\alpha]_D^{20}$	$[\alpha]_{BG}^{20}$	$[\alpha]_B^{20}$
° C.				
90	+5.88	+5.72	+4.43	+0.34
70	5.06	4.78	3.26	-1.68
50	4.02	3.54	1.74	-4.03

Ethylic Tartrate.—Fortunately Winther has supplied very complete data for this substance.* The characteristic diagram is given in fig. 5; some of the points have been omitted, as they come so close together. Excepting those for solutions in water, the values all lie very close indeed to straight lines. The solution in benzene (not included) also appears to afford slightly exceptional values.

2-Nitrotoluene-4-sulphonyltetrahydroquinidine.—The characteristic diagrams

* *Op. cit.*, vol. 60, p. 582.

of this substance are given in fig. 6. It will at once be obvious that it differs in a marked degree from those previously constructed and does not correspond with any of the ideal cases that have been discussed. Apparently, in solutions of this substance, the dispersion is not a function of the rotatory power and there is a second independent variable concerned.

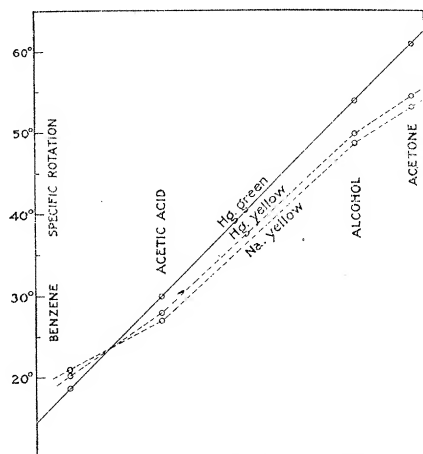
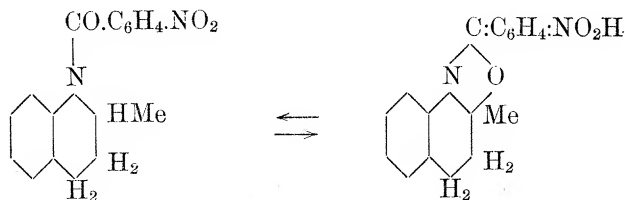


FIG. 6.—2-nitrotoluene-4-sulphonyl-1-tetrahydroquinaldine. Equilibrium varied by change of solvent at constant temperature 20° C.

An Explanation of Anomalous Rotatory Dispersive Power.

The question to be considered is what two substances of opposite rotatory power and different rotatory dispersive power are likely to exist in cases such as those under consideration. Taking into account the views one of us has long held in regard to the origin of colour, as orthonitrobenzoyltetrahydroquinaldine is a yellow substance, it appears not improbable that it may exist in solution in two isodynamic forms, viz.:—



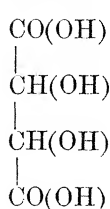
Being quinonoid, the second of these would doubtless be the more dispersive.

Passing to tartaric acid, we have to account for the fact that the rotatory power of the acid and of its ethereal salts is more or less affected by variation in the temperature; moreover, that not only water but also "neutral" solvents

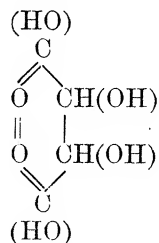
modify this rotatory power, often to a considerable extent; and that the rotatory dispersive power of the solutions is generally anomalous. According to Biot, no such abnormal dispersive power is noticeable in solutions of the metallic tartrates; this statement has been confirmed by Winther.

Although it has been customary to regard carboxylic acids as compounds containing the free carboxylic radicle, the evidence that such is always the case is in no way sufficient, let alone conclusive. The behaviour of monocarboxylic acids, especially their recognised tendency to form double molecules, as in the case of acetic acid, is clear proof that the carboxylic radicle is far from being saturated.

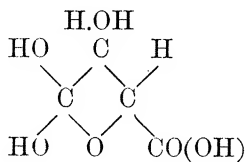
Taking into account the views that now prevail that valency has direction and the conclusion which is the outcome of this conviction that carbon atoms are not united as mere links in a chain but tend to form re-entering systems, such systems being formed preferentially from either five or six atoms; moreover, that oxygen atoms may take the place of carbon atoms: it is both possible and probable that the fundamental molecule of tartaric acid can exist not only in the "open" form commonly pictured (I) but also in various isodynamic "closed" forms (II, III and IV):—



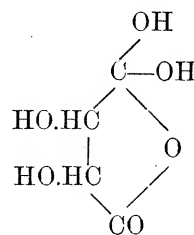
I.



II.



III.



IV.

It cannot be denied that there is little to guide us in choosing between these formulæ or in deciding which is the most likely form to preponderate.*

The third obviously bears a marked resemblance to that of fructose—in which, in place of the four-membered (tetraphane) ring there is a five-membered (pentaphane) ring. The fourth is similar to the third.

It is scarcely probable, we think, either that any alteration in the degree of hydration of a substance represented by formula I or that the passage from

* It is remarkable that possibilities such as these have not been taken into account by Walden, who has recognised that structural changes may in some cases underlie the alterations in rotatory power observed in solutions (*op. cit.*, p. 407). Taking the ethereal salts of tartaric acid as an example, he has postulated changes which appear to us not only to be improbable, but altogether insufficient to account for the magnitude of the effects observed, especially the change in sign of the rotatory power, accompanied by a sufficient difference in dispersive power to give rise to the phenomenon of anomalous

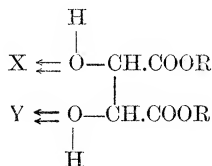
form I into form II would be attended with an alteration in the sign of the rotatory power such as is known to take place in solutions of tartaric acid; and on general grounds the second is scarcely a probable form.

We believe the known facts are best accounted for on the assumption that forms I and III are the two modifications in equilibrium in most cases and that form III is the more stable at lower temperatures and in concentrated solutions, the carboxylic form at higher temperatures and in weaker solutions: if this be the case, the lactonic form is the more dispersive and of lower rotatory power.

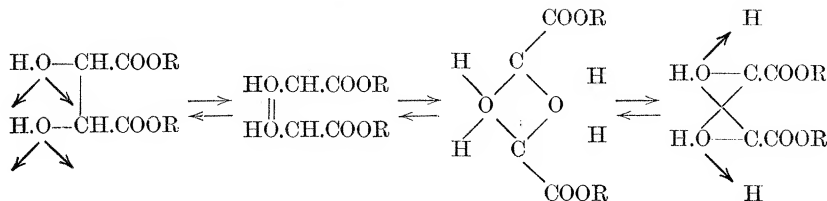
It is to be expected that metallic salts would exist as carboxylates: the normal behaviour of metallic tartrates is therefore such as might be expected from the point of view of our hypothesis.

Form IV appears to us to be less probable than III on various grounds.

dispersion. The changes which Walden pictures as possible are conveyed by the following symbols:—



(X and Y may be either other molecules of the tartrate or molecules of the solvent.)



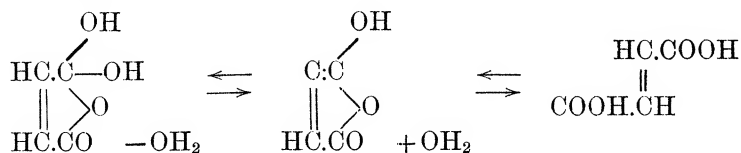
It is well known that gluconic and similar acids derived from the sugars are very readily converted into the corresponding lactones—a change precisely similar to that attending the conversion of the carboxylic form of tartaric acid into the tetraphane form; and if gluconic lactone be regarded as present in solution in a hydrated form, the behaviour of the two acids is in correspondence. Gluconic and similar lactones, moreover, have high rotatory powers, whilst the acids derived from them have low rotatory powers of opposite sign—which is precisely the difference we have postulated in the case of the two isodynamic forms of tartaric acid.

It may also be pointed out here that in the case of the ethereal salts of tartaric acid two stereoisomeric modifications of the tetraphane and pentaphane forms are possible: this is also true of the quinonoid form of the *o*-nitroquinaldine derivative examined by Pope and Winmill. As “asymmetric influences” are likely to be operative in such cases, the proportions in which the two isomerides are in equilibrium may be very different and one form prevail to the almost entire exclusion of the other.

A similar formula has been suggested for maleic acid in contradistinction to the dicarboxylic formula assigned to the isomeric fumaric acid



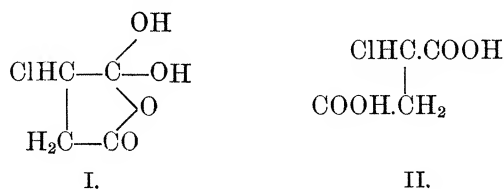
Such a formula is justified not only by the fact that maleic and fumaric acids differ considerably in strength but especially because maleic acid is converted into fumaric acid by mere contact with chlorhydric or bromhydric acid—a change which is easily accounted for by the assumption of this formula but with difficulty in any other way.



If therefore tartaric acid existed in form IV under ordinary conditions, it is to be expected that it would be easily converted into its optical isomeride; actually this change only takes place under special conditions and at relatively high temperatures.

Malic acid resembles tartaric acid in its optical behaviour and a similar explanation may be given of its peculiarities. It is in accordance with our hypothesis that the rotatory power of methoxysuccinic acid, $\text{COOH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OMe}) \cdot \text{COOH}$, is subject to but slight variation, as the formation from this compound of a closed tetraphane system corresponding to form III of tartaric acid is impossible; it is nevertheless conceivable that the two compounds *in esse* in the original substance may both give rise to the corresponding derivative: but this argument would not apply to the case of chlorosuccinic acid, for example.

In this latter case, however, two forms are still possible, related to one another as are maleic and fumaric acids, viz.,

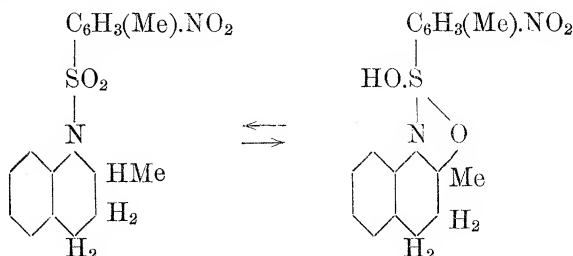


It is well known that the acid chloride derived from succinic acid has a

constitution corresponding to formula I and it is by no means improbable that a solution of the acid in large part consists of molecules of this type.

It is obvious that much may yet be learnt by the thorough optical study of active derivatives of succinic acid and by contrasting their optical characters with their behaviour as acids.

The exceptional behaviour of the orthonitrotoluenesulphonyl-derivative described by Pope and Winnill may be explained on the assumption that it undergoes change into an isomeric form, of which two stereoisomeric modifications are possible.



The hypothesis now advocated may be applied in other cases, for example, perhaps in explanation of the great difference in rotatory power of the ortho-substituted derivatives of menthylic alcohol in comparison with the isomeric meta- and para-compounds and of similar differences among the glycerates.

In view of the well known fact that the rotatory power is often considerably affected by the solvent, it may appear surprising that diagrams should be obtained which are so closely in accord with the assumption we have made that only two optically active constituents are in equilibrium and that these have constant rotatory power. Although an irregular or sudden variation in the rotatory power of any component of the solution would inevitably give rise to corresponding irregularities in the characteristic diagram if the substance came under cases II or IV, the variation might not be apparent if the factors influencing the equilibrium were equally concerned in the changes in rotatory power.

The result at which we have arrived—that if the rotatory power of a substance in solution be observed, whatever the variation in the conditions, the observations in light of any particular refrangibility, as a rule, can all be located upon the same straight line in the characteristic diagram—appears to us to be of deep significance, as indicating a relationship among solvents generally, underlying their action towards substances generally, of a very definite and regular character: each solvent would appear to have its definite

sphere and mode of action, so that any two solvents behave relatively always in the same way towards solutes generally, apart from the exceptional cases in which some special property of the solute comes into operation to disturb this regularity of action.*

It is noteworthy that although the rotatory power of each substance varies considerably in ten of the twelve cases brought forward by Pope and Winmill the dispersive power of each set of solutions is practically identical.

By considering the behaviour of solvents generally and by further study of cases such as that afforded by the orthonitroparasulphonyl-derivative frequently referred to, in which case the activity of benzene as a solvent is quite out of the normal order, we hope that we shall be able to throw further light on this part of our subject. But taking into account the numerous factors involved, the equilibrium arrived at in each case cannot well be other-wise than the outcome of a variety of changes which balance one another. It is not likely, therefore, that a simple solution of the problem can be found. The difficulty is all the greater because of the difficulty of arriving at any proper basis of comparison. Hitherto it has been customary to contrast the values arrived at by observations made in light of the refrangibility of the sodium line but this is obviously insufficient; even, however, when the observations are extended to rays of other refrangibilities, it is possible that the difficulty of making proper comparisons met with in the case of other physical properties will still not be overcome.

To state our views, in a few words:—

The variations in rotatory power met with in optically active compounds may be ascribed (*a*) to alterations in molecular size and to the formation of compounds between solvent and solute; (*b*) to the occurrence of changes giving rise to the presence of reversibly related isodynamic forms.

The changes included under (*a*) are common to all optically active substances; those included under (*b*) can occur only in special cases. In these special cases, if the change involve the formation of compounds so different in chemical type that they not only differ in rotatory power in sign but also in rotatory dispersive power, the product might have anomalous dispersive power; in other cases, it would behave normally.

* *Cp.* Winther, *op. cit.*, vol. 60, p. 702; Walden, *op. cit.*, p. 397.